



## Electrocatalytic dechlorination of volatile organic compounds at a copper cathode. Part I: Polychloromethanes

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### ABSTRACT

The electrochemical reductive dehalogenation of  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{Cl}$  was investigated at Cu in dimethylformamide (DMF). The principal aim of the study was to check whether Cu has good electrocatalytic properties and is stable to fouling in preparative-scale electrolyses. All polychloromethanes (PCMs) have been investigated by cyclic voltammetry in  $\text{DMF} + 0.1 \text{ M } \text{Pr}_4\text{NBF}_4$  in order to evaluate the reduction mechanism and the catalytic activity of Cu. The electrochemical reduction of  $\text{CCl}_4$  and  $\text{CHCl}_3$  has also been studied by controlled-potential electrolysis in  $\text{DMF} + 0.1 \text{ M } \text{Pr}_4\text{NBF}_4$  both in the absence and presence of  $\text{H}_2\text{O}$  or  $\text{CH}_3\text{CO}_2\text{H}$ , using chromatographic techniques to determine the intermediates and final products of the process. Cu exhibits a good electrocatalytic activity, in some cases the positive shifts of the reduction potentials with respect to GC being comparable with those at Ag, which is considered to be one of the best candidates for environmental applications in dehalogenation reactions. The results point out that the reduction mechanism at Cu is similar to what was already observed for Ag on which reduction of PCMs takes place through two competing reaction pathways: hydrodehalogenation and hydrogenolysis of carbenes. The proton availability of the medium affects drastically both the catalytic effect of Cu and the distribution of reduction products. The presence of an added proton donor promotes the hydrodehalogenation pathway, enhancing the concentration of intermediate PCMs and the final yield of methane, which is the main product of the exhaustive electrolysis.

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### 1. Introduction

Volatile organic compounds (VOCs) represent one of the most undesirable classes of contaminants because of their great mobility and tendency to accumulate in closed spaces [1]. Among VOCs, halogenated compounds (HVOCs) such as polychloromethanes (PCMs), polychloroethanes and polychloroethylenes represent a particularly dangerous group due to their toxic and carcinogenic character [2] and for their undesirable activity in the depletion of ozone in the Arctic region [3]. The conventional methods employed for the removal of HVOCs cannot be considered definitive because they consist principally in the simple transfer of pollutants from one phase to another, using sequestering agents such as carbon sieves, which then require further treatment or appropriate disposal in a second stage. For this reason, the development of new technologies for their destruction has been widely investigated; these include thermal decomposition [4], catalytic oxidation [5], UV oxidation [6], procedures using thermal plasma [7], ozonization [8],

degradation on  $\text{TiO}_2$  [9,10], electrochemical oxidation [11], chemical [12] and electrochemical [13] reduction and, more recently, sonochemical treatments [14] and combined electrochemical oxidation-reduction processes [15].

A principal drawback of several methodologies that involve the formation of highly reactive radical species is low selectivity toward the desired degradation product. This is the case, for example, of UV irradiation or BDD electrooxidation, whereby undesirable byproducts are uncontrollably formed. On the other hand, biological treatments are really time-consuming and less tolerant to the toxicity of the organic halides and/or their partially dechlorinated products, resulting in a loss of efficiency. On the contrary, reductive dehalogenation methods, particularly electrochemical reduction, represent a very promising approach, being intrinsically milder, more selective and easier to run than most of the other methodologies mentioned above.

The electrochemical destruction of HVOCs has been extensively studied in aqueous solutions [16–26] and in aqueous-aprotic solvent mixtures [27,28], at various electrode materials, mainly metals [18–20], graphite and composites [21–26]. However, the relatively low solubility of HVOCs in water and the very negative potentials required for their reduction at the most common electrode

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materials result in abundant H<sub>2</sub> generation, long treatment duration and a drastic decrease of current efficiency. In contrast to water, these compounds are highly soluble in organic solvents and their electroreduction often occurs well before the cathodic limit of many non-aqueous electrolytes. Therefore, highly concentrated solutions can be prepared and electrolyzed with high current densities. This means that great amounts of chlorinated VOCs may be transformed to less dangerous, more desirable products in a reasonably short period of time. Some papers report the partial or complete dechlorination of CCl<sub>4</sub> [29], CHCl<sub>3</sub> [30], CH<sub>2</sub>Cl<sub>2</sub> [31], CF<sub>2</sub>Cl<sub>2</sub> [32,33] and CCl<sub>2</sub>CHCl [34] in organic solvents such as CH<sub>3</sub>CN or in aqueous-alcoholic solutions. Furthermore, it has been proved that PCMs can be successfully dechlorinated to methane in DMF containing a good proton donor such as CH<sub>3</sub>CO<sub>2</sub>H [13].

The electrochemical method of dechlorination is attractive as a preventive tool to be applied to the destruction of existing stocks of banned chlorinated VOCs or those which are produced as byproducts in some industrial processes. It can also be applied for the treatment of water pollutants once these are extracted from water either by adsorption on activated carbon or by air-stripping. However, a major issue to be resolved in the perspective of developing this method into a feasible technology is the need for electrodic materials with long working life, high catalytic activity and affordable market price in order to reduce investment and operating costs. In fact, the use of precious metals such as Pd and Pt in large scale applications is not very attractive for economic reasons.

A variety of electrodic materials have been investigated for the electrochemical reduction of HVOCS in non-aqueous solvents, some of them, especially Ag, showing good catalytic properties both in terms of current efficiency and selectivity. The electrocatalytic reduction of organic halides has been extensively investigated at Ag from different viewpoints and some crucial aspects of the mechanism are by now well understood [35–41]. On the contrary, the electrocatalytic properties of Cu in organic solvents have not yet been exploited, in particular for environmental applications, and little is known also about the kinetics and mechanism of the electroreduction process, although some examples have been reported in both aqueous [16] and non-aqueous solutions [35].

Herein, we describe the electrocatalytic behavior of Cu toward the hydrodechlorination of PCMs (CCl<sub>4</sub>, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>Cl) of general formula CH<sub>n</sub>Cl<sub>(4-n)</sub> ( $n = 0–3$ ) in dimethylformamide (DMF). For the sake of comparison, glassy carbon (GC) is also considered because it is the best approximation to a non-catalytic surface [42].

Since hydrodehalogenation involves both electron and proton transfers, it is helpful to be able to control both of them. To this end, use of an aprotic solvent such as DMF appears to be the best choice for mechanistic investigations. Furthermore, H<sub>2</sub>O and acetic acid (HAc) have been considered as proton donors to be added to the solution for a better understanding of how the proton availability in the medium may influence the dechlorination mechanism and the product distribution. Some of the conclusions drawn from the results of this study may be of great help to understand what happens in aqueous electrolytes, although addition of H<sub>2</sub>O or HAc to DMF is only a far approximation of a protic solvent.

## 2. Experimental

### 2.1. Chemicals

DMF (WWR, 99%) was treated with anhydrous Na<sub>2</sub>CO<sub>3</sub> and doubly distilled at reduced pressure under N<sub>2</sub> atmosphere. Tetrapropylammonium tetrafluoroborate (Pr<sub>4</sub>NBF<sub>4</sub>) (Fluka, >98%) was recrystallized twice from EtOH and dried in a vacuum oven at 70 °C. CCl<sub>4</sub>, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>Cl were high purity reagents

purchased from Sigma–Aldrich and were used without further purification.

### 2.2. Electrochemical instrumentation

Electrochemical measurements were performed on a computer-controlled EG&G PARC Model 273A potentiostat equipped with a digital coulometer. Cyclic voltammetry experiments were carried out in a three-electrode cell with a glassy carbon disc or a copper disc as working electrode. The counter electrode and the reference electrode were a Pt wire and Ag|AgCl|Me<sub>4</sub>NCl(sat) in CH<sub>3</sub>CN/DMF 3/1, respectively. The latter was calibrated after each experiment against the ferrocenium/ferrocene couple. The potentials measured against the Ag|AgCl|Cl<sup>–</sup> reference electrode were converted to the SCE scale, to which all potentials in the paper are referred, by using  $E_{Fe^{2+}/Fe}^{\theta} = 0.475$  V vs. SCE in DMF. The working electrodes were built from a 3 mm diameter GC rod (Tokai GC-20) or from a 2 mm diameter Cu wire (Alfa Aesar, 99.999%) and were cleaned and activated prior to each experiment as previously described [35]. Controlled-potential electrolyses were carried out in a divided cell at a Cu cylinder of 9.5 cm<sup>2</sup> area, using a Pt foil as a counter electrode and Ag|AgCl|Cl<sup>–</sup> as a reference electrode. Throughout the electrolysis experiments reported in this paper a single Cu working electrode was used, which showed to be always catalytically active regardless of the number of experiments or their durations. All experiments were carried out at 25 °C.

### 2.3. Analytical methods

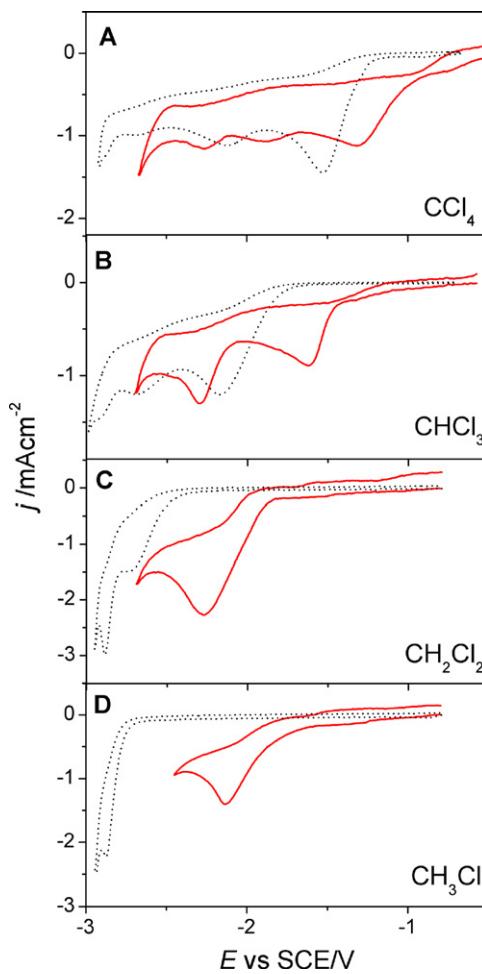
Electrolysis products were analyzed using an HP 6890 gas chromatograph equipped with an HP 5973 mass selective detector (MS) or a flame ionization detector (FID) (Agilent Technologies). Products in the liquid phase were analyzed as headspace samples on a DB-5ms 30 m × 0.25 mm × 0.25 μm capillary column using the MS detector, whereas an HP Plot Q 30 m × 0.537 mm × 0.40 μm capillary column and the FID detector were used for the analysis of the gaseous products (see [Supplementary information](#) for more details). Authentic compounds were used for the identification and quantification, via calibration curves, of all products.

## 3. Results and discussion

### 3.1. Cyclic voltammetry

The electrochemical reduction of PCMs at GC in DMF + 0.1 M Et<sub>4</sub>NBF<sub>4</sub> has already been investigated in depth, both in the presence and absence of a proton donor [35,37]. Since, however, in this study Pr<sub>4</sub>NBF<sub>4</sub> was used as supporting electrolyte instead of Et<sub>4</sub>NBF<sub>4</sub>, it is helpful to reconsider the voltammetric behavior of the substrates at GC for a more sound comparison with Cu. In fact, it is well known that the length of the alkyl chain in the R<sub>4</sub>N<sup>+</sup> cations influences the reduction potentials of alkyl halides [43,44] and therefore the results recorded with different supporting electrolytes are not directly comparable. For the present study, Pr<sub>4</sub>NBF<sub>4</sub> has been preferred to Et<sub>4</sub>NBF<sub>4</sub> because, in the presence of a strong base such as electrogenerated carbanions, tetraalkylammonium cations R<sub>4</sub>N<sup>+</sup> often undergo Hoffman degradation to an alchene R(–H) and R<sub>3</sub>N. Thus, the presence of Et<sub>4</sub>NBF<sub>4</sub> might produce ethylene, which is one of the possible products of PCMs degradation in case of coupling reactions. This possibility is obviously avoided in the case Pr<sub>4</sub>NBF<sub>4</sub> is employed as supporting electrolyte.

Cyclic voltammograms of CCl<sub>4</sub>, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>Cl at GC and Cu in DMF + 0.1 M Pr<sub>4</sub>NBF<sub>4</sub> are shown in [Fig. 1](#). At GC each compound exhibits a series of irreversible reduction peaks equaling in number that of the chlorine atoms present in the molecule.



**Fig. 1.** Cyclic voltammetry of  $\text{CH}_n\text{Cl}_{(4-n)}$  in DMF + 0.1 M  $\text{Pr}_4\text{NBF}_4$  at Cu (solid line) and GC (dotted line) electrodes;  $v = 0.2 \text{ V s}^{-1}$ ;  $c = 2 \text{ mM}$ .

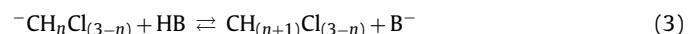
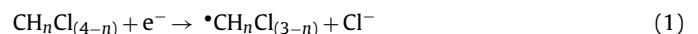
Instead, at Cu each PCM containing  $z$  chlorine atoms ( $z \geq 2$ ) shows  $z - 1$  irreversible reduction peaks. When several peaks are present, the first one is more intense than the others, especially in the case of  $\text{CCl}_4$  and  $\text{CHCl}_3$  at GC. A comparison between the voltammograms reported in Fig. 1, especially at GC, shows that reduction of each compound involves the intermediate formation of less chlorinated substrates. Thus,  $\text{CCl}_4$  is first reduced to  $\text{CHCl}_3$ , then to  $\text{CH}_2\text{Cl}_2$  and then to  $\text{CH}_3\text{Cl}$ , which is finally reduced to  $\text{CH}_4$ .

The presence of a good proton donor modifies the voltammetric responses of all PCMs. Cyclic voltammograms recorded at both electrodes in the presence of acetic acid (HAc) or  $\text{H}_2\text{O}$  are reported in the Supplementary information (Figs. S1 and S2). The most prominent effect of the acid regards the peak currents of  $\text{CCl}_4$  and  $\text{CHCl}_3$ . In the presence of  $z$  equivalents of HAc ( $z = 4, 3, 2, 1$  for  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CH}_3\text{Cl}$ , respectively), each compound shows a series of peaks of equal height at both GC and Cu. Similar results were obtained by using  $\text{H}_2\text{O}$  as a proton donor; in this case, however, a large excess (0.4 M) is required since  $\text{H}_2\text{O}$  is a much weaker proton donor than acetic acid. The peak potentials measured for all compounds in the absence and presence of proton donors are summarized in Table 1. Besides the first peak, which certainly corresponds to the reduction of the starting PCM, data for all other successive peaks are reported for all compounds. A comparison between the data clearly shows that reduction of each PCM at GC occurs by a hydrodechlorination mechanism in which a series of dechlorinated compounds are obtained as intermediates. The compounds undergo hydrodechlorination also at Cu but the sequence at this electrode is not as obvious as at GC. Indeed, at Cu each PCM shows  $z - 1$  peaks rather

than  $z$  peaks expected for complete sequential hydrodechlorination of a compound containing  $z$  chlorine atoms. This discrepancy can be explained by comparing the peak potentials of  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{Cl}$ . As shown in Table 1 (entries 3 and 4) reduction of  $\text{CH}_3\text{Cl}$  at Cu occurs at potentials 0.13–0.35 V more positive than that of  $\text{CH}_2\text{Cl}_2$  at the same electrode. Therefore, even though reduction of PCMs at Cu follows a hydrodechlorination mechanism, a separate peak for  $\text{CH}_3\text{Cl}$  cannot be observed in the voltammograms of  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$  simply because it is covered by the reduction peak of  $\text{CH}_2\text{Cl}_2$ . This inversion of reduction potential order for  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{Cl}$  has been observed also in a previous investigation at Ag [13,37].

A major difference between the processes at the two electrodes regards the potentials at which reduction of  $\text{CH}_n\text{Cl}_{(4-n)}$  occurs. As shown in Table 1, for all PCMs values of  $E_p$  measured at Cu are significantly more positive than those obtained at GC, indicating that Cu possesses electrocatalytic properties toward the reduction of carbon–chlorine bonds. Table 1 (columns 9–11) reports the electrocatalytic activity,  $\Delta E_p^{\text{cat}}$ , of Cu measured in different conditions.  $\Delta E_p^{\text{cat}} = E_p^{\text{Cu}} - E_p^{\text{GC}}$  is defined as the anodic shift of the peak potential at Cu ( $E_p^{\text{Cu}}$ ) with respect to GC, which is considered to be the best approximation to a non-catalytic system. In the absence of added proton donors, the catalytic effect varies from about 0.2 V for  $\text{CCl}_4$  to more than 0.7 V for  $\text{CH}_3\text{Cl}$ . Interestingly, the electrocatalytic activity of Cu is further enhanced by the presence of acetic acid or  $\text{H}_2\text{O}$ , which shifts the reduction peaks to even more positive potentials (Table 1, columns 10 and 11).

The reduction mechanism of PCMs at GC both in the absence and presence of a proton donor has recently been described in detail [37]. The data reported here agree very well with the conclusions of the previous study; reduction of each PCM occurs through a series of reduction steps each involving two electron transfers, removal of a chloride ion and protonation. For example, in the case of  $\text{CCl}_4$ , a concerted dissociative electron transfer to the substrate yields a trichloromethyl radical and a chloride ion; this is then followed by  $1 \text{ e}^-$  reduction of the radical and protonation of the ensuing carbanion to give  $\text{CHCl}_3$ . In general, for any PCM ( $\text{CH}_n\text{Cl}_{(4-n)}$ ) ( $n = 0–3$ ) we may write:



where HB stands for any proton donor present in solution.

If the applied potential is negative enough to ensure electroreduction of all chlorinated methanes, the same pattern is repeated again and again until  $\text{CH}_4$  is formed. However, it has been observed that other reaction pathways compete with the hydrodechlorination sequence, especially in the absence of a good proton donor [13,37]. These may involve either the radical  $\cdot\text{CH}_n\text{Cl}_{(3-n)}$  or the carbanion  $\text{CH}_n\text{Cl}_{(3-n)}^-$  or both of them. A possible reaction of  $\text{CH}_n\text{Cl}_{(3-n)}^-$ , in competition with protonation, is expulsion of  $\text{Cl}^-$  to give a carbene.



In the case of Cu, a comparison between the voltammetric data obtained in the presence of a proton donor indicates that the principal reduction pathway is through the sequence of reactions (1)–(3), which is in line with what has been observed at GC. Instead, the voltammetric data recorded in the absence of added proton donors show some differences between the behaviors of the two electrode materials. In particular, the carbene route seems to have some importance in the case of Cu. In any case, the first step of the reduction process is a concerted dissociative

**Table 1**

Reduction potentials of polychloromethanes (2 mM) in DMF + 0.1 M  $\text{Pr}_4\text{NBF}_4$  measured at  $v = 0.2 \text{ V s}^{-1}$  in the absence and presence of  $\text{H}_2\text{O}$  or acetic acid, HAc.<sup>a</sup>

Entry	Substrate	GC			Cu			$\Delta E_p^{\text{cat}}$		
		$E_p$	$E_p^{(\text{HAc})}$ <sup>b</sup>	$E_p^{(\text{H}_2\text{O})}$ <sup>c</sup>	$E_p$	$E_p^{(\text{HAc})}$ <sup>b</sup>	$E_p^{(\text{H}_2\text{O})}$ <sup>c</sup>	–	HAc	$\text{H}_2\text{O}$
1	$\text{CCl}_4$	–1.53	–1.52	–1.50	–1.32	–1.08	–1.22	0.21	0.44	0.28
		–2.12	–2.19	–2.11	–1.88	–1.50	–1.78			
		–2.69	–2.71	–2.65	–2.27	–2.30	–2.16			
		–2.88	–2.95	–2.88						
2	$\text{CHCl}_3$	–2.17	–2.14	–2.15	–1.62	–1.45	–1.75	0.55	0.69	0.43
		–2.60	–2.64	–2.63	–2.30	–2.31	–2.23			
		–2.92	–2.91	–2.81						
3	$\text{CH}_2\text{Cl}_2$	–2.74	–2.70	–2.69	–2.28	–2.29	–2.16	0.46	0.41	0.53
		–2.88	–2.88	–2.69						
4	$\text{CH}_3\text{Cl}$	–2.87	–2.93	–2.91	–2.14	–1.94	–2.03	0.73	0.99	0.88

<sup>a</sup> All potentials are in V vs. SCE; values for the first peak, second peak, etc., are listed for each compound.

<sup>b</sup> Measured in the presence of  $z$  equivalents of acetic acid;  $z$  = number of chlorine atoms in  $\text{CH}_n\text{Cl}_{(4-n)}$ .

<sup>c</sup> Measured in the presence of 0.4 M  $\text{H}_2\text{O}$ .

<sup>d</sup>  $\Delta E_p^{\text{cat}} = E_p^{\text{Cu}} - E_p^{\text{GC}}$ , where  $E_p^{\text{Cu}}$  and  $E_p^{\text{GC}}$  stand for peak potentials measured at Cu and GC, respectively.

electron transfer (ET), i.e. ET and C–Cl bond rupture occur in a single step (Eq. (1)). The concerted mechanism is confirmed for all PCMs by values of transfer coefficient,  $\alpha$ , close to 0.3 [35]. The intermediate radical  $\cdot\text{CH}_n\text{Cl}_{(3-n)}$  is more easily reducible than the parent  $\text{CH}_n\text{Cl}_{(4-n)}$  molecule; it is therefore immediately reduced to  $\text{CH}_n\text{Cl}_{(3-n)}$ , which is rapidly protonated by any proton donor present in solution. If a good proton source is available in the reaction medium, the overall reaction mechanism could be considered as a set of consecutive hydrodechlorination steps each of which involves the consumption of one  $\text{H}^+$  and  $2\text{e}^-$  and the loss of one  $\text{Cl}^-$  as exemplified by reactions (1)–(3). The end product of this cyclically repeating hydrodechlorination process is methane.

In conclusion, PCMs have shown a voltammetric behavior at Cu similar to that at Ag both in the absence and presence of a proton donor. This is indicative that the dehalogenation mechanism is similar at both electrodes. Furthermore, a comparison of the  $\Delta E_p^{\text{cat}}$  for Cu electrode with those for Ag indicates that the two electrodes show also comparable electrocatalytic effects both in the absence and presence of HAc or  $\text{H}_2\text{O}$  (Fig. 2).

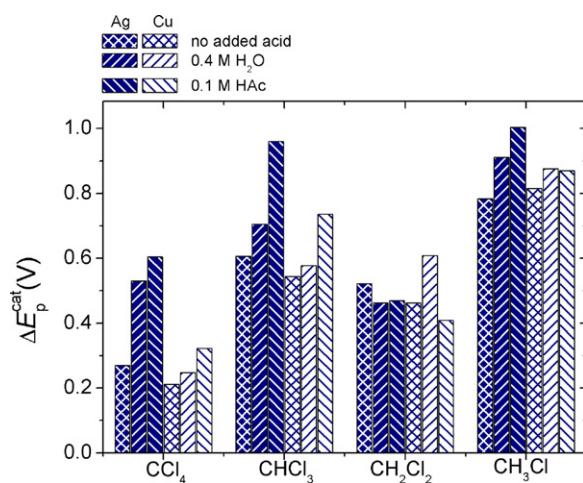
On the basis of the voltammetric analysis Cu is a good electrode material for the reduction of C–Cl bonds and is thus a potential candidate for the hydrodehalogenation of polychloromethanes under mild conditions.

### 3.2. Controlled-potential electrolyses

The voltammetric data in DMF, especially in the presence of an acid show that it is possible to reduce selectively  $\text{CCl}_4$  and all less chlorinated compounds arising from its reduction, by operating under potentiostatic conditions. Furthermore, Cu shows an excellent catalytic activity, especially when a good proton donor is added in solution. The addition of a proton source not only helps lowering the overpotential of the electrochemical process but also increases the selectivity of the reaction toward hydrodechlorination products. To have a confirmation that Cu can be employed in the degradation of H VOCs, we have carried out some electrolysis experiments on  $\text{CCl}_4$  and  $\text{CHCl}_3$  in different conditions and determined all  $\text{C}_1$  and  $\text{C}_2$  products by chromatographic analyses. A particular aim of these experiments was to verify whether the activity of Cu changes during electrolysis due to possible fouling induced by interactions of intermediates and products with the electroodic surface.

The results of preparative-scale electrolyses of  $\text{CCl}_4$  and  $\text{CHCl}_3$ , performed at a Cu cathode, in the absence and presence of HAc or  $\text{H}_2\text{O}$ , are summarized in Tables 2 and 3. The experiments were conducted under potentiostatic conditions and the applied potential,  $E_{\text{app}}$ , was periodically shifted to more negative values during the experiment in order to reduce selectively the starting compound and its reduction products. Comparative experiments were also carried out at a fixed potential corresponding to that of the most cathodic peak of each substrate. Conversion of  $\text{CCl}_4$  and  $\text{CHCl}_3$ , as well as production of partially dechlorinated compounds, was monitored by cyclic voltammetry. Based on voltammetric responses, the applied potential was always changed when the concentration of the species mainly undergoing reduction dropped to less than 20% of its starting value. This rule was not applied in the last stage of the electrolysis, which was made almost exhaustive, a complete stop being carried out after the current has dropped to  $<5\%$  of its initial value, which often corresponded to a reagent conversion  $>95\%$ .

Fig. 3a–c shows variations of the principal reduction products of  $\text{CCl}_4$  recorded during preparative electrolyses at Cu in DMF + 0.1 M  $\text{Pr}_4\text{NBF}_4$  performed in the absence or presence of an added proton source. In each case, the electrolysis was carried out at three different applied potentials, corresponding to the reduction of  $\text{CCl}_4$ ,  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$ , respectively (Table 2). During electrolysis accumulation of  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  as reaction intermediates was observed, while  $\text{CH}_4$  was always formed as the final reduction product. Interestingly, accumulation of  $\text{CH}_3\text{Cl}$  was not observed, its maximum detected concentration being less than 1%. This is in line with the fact that  $\text{CH}_3\text{Cl}$  is easier to reduce than  $\text{CH}_2\text{Cl}_2$  and



**Fig. 2.** Catalytic activities of Ag and Cu, expressed as  $\Delta E_p^{\text{cat}} = E_p^{\text{M}} - E_p^{\text{GC}}$  (where  $\text{M} = \text{Ag}$ , Cu), for the reduction of  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{Cl}$  in DMF + 0.1 M  $\text{R}_4\text{NBF}_4$ ; data for Ag taken from reference [37].

**Table 2**Electrolysis of  $\text{CCl}_4$  (10 mM) in 20 mL DMF + 0.1 M  $\text{Pr}_4\text{NBF}_4$  at a Cu cathode.<sup>a</sup>

Entry	Substrate	$E_{\text{app}}^{\text{b}}$ (V)	$n^{\text{c}}$	$\text{CCl}_4$ (%)	$\text{CHCl}_3$ (%)	$\text{CH}_2\text{Cl}_2$ (%)	$\text{CH}_3\text{Cl}$ (%)	$\text{CH}_4$ (%)	$\text{C}_2^{\text{d}}$ (%)	$(\text{C}_1)_{\text{tot}}^{\text{e}}$ (%)
1a	$\text{CCl}_4$	−1.60	1.70	27.9	20.8	1.6	0.0	0.0	0	50.3
1b		−2.00	2.70	6.5	11.1	3.3	0.1	0.7	0.2	21.7
1c		−2.65	4.70	0.0	0.0	0.0	1.0	5	1.6	6.0
2	$\text{CCl}_4$	−2.65	1.0	63.2	14.9	4.1	0.0	1.2	0.2	83.4
		−2.65	3.0	0	20.1	1.7	0.3	8.0	1.0	30.1
		−2.65	4.0	0.0	0.0	0.0	0.2	9.6	1.8	9.8
3a	$\text{CCl}_4 + \text{H}_2\text{O}^{\text{f}}$	−1.40	1.8	2.4	71.3	7.3	0.0	0.1	0	81.1
3b		−2.00	3.82	0.0	0.0	52.2	1.0	8.7	1	61.9
3c		−2.35	8.11	0.0	0.0	0.0	0.0	21.4	1.4	21.4
4	$\text{CCl}_4 + \text{H}_2\text{O}^{\text{f}}$	−2.35	1.26	44.7	29.4	12.2	2.5	1.4	0.2	90.2
		−2.35	3.78	2.4	6.3	28.2	1.9	11.9	0.6	50.7
		−2.35	7.59	0	0	3.8	0.7	33.4	0.8	37.9
		−2.35	10.21	0	0	0	0	36.7	0.8	36.7
5a	$\text{CCl}_4 + \text{HAc}^{\text{g}}$	−1.25	2.01	4.0	74.4	5.2	0.0	0.2	0.4	83.8
5b		−1.80	4.29	0.0	2.1	78.0	0.2	1.5	0.4	81.8
5c		−2.40	9.32	0.0	0.0	9.7	0.9	70.0	1.8	80.6
6	$\text{CCl}_4 + \text{HAc}^{\text{g}}$	−2.40	2.1	34.0	36.4	21.2	0.8	5.6	1.4	98.0
6		−2.40	4.1	8.9	26.6	44.1	0.9	13.8	3.0	94.3
6		−2.40	6.1	1.8	8.8	53.4	1.5	22.2	3.6	87.7
6		−2.40	10.5	0.0	0.0	0.0	1.8	62.6	4.2	4.4

<sup>a</sup> Values in percentage were calculated with respect to the starting substrate.<sup>b</sup> Applied potential vs. SCE.<sup>c</sup> Electrons transferred per molecule.<sup>d</sup>  $\text{C}_2$  stands for the sum of  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{H}_4$ .<sup>e</sup> Mass balance for  $\text{C}_1$  compounds with respect to initial substrate.<sup>f</sup> In the presence of 0.4 M  $\text{H}_2\text{O}$ .<sup>g</sup> In the presence of 0.1 M HAc.

hence cannot accumulate because the two compounds are concomitantly reduced at the applied potential ( $E_{\text{app}} < -2.35$  V). The yields of the intermediates and the final product strongly depend on the proton availability of the reaction medium. In the absence of any added proton donor, the maximum yields of  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  were 20.8% and 3.3%, respectively, whereas the final yield of  $\text{CH}_4$  was only 5% (Table 2, entries 1a–c). Both the final  $\text{CH}_4$  production and the yields of the intermediates were found to increase in the presence of 0.4 M  $\text{H}_2\text{O}$ . In this circumstance the maximum yields of  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  rose to 71.3% and 52.2%, respectively, while

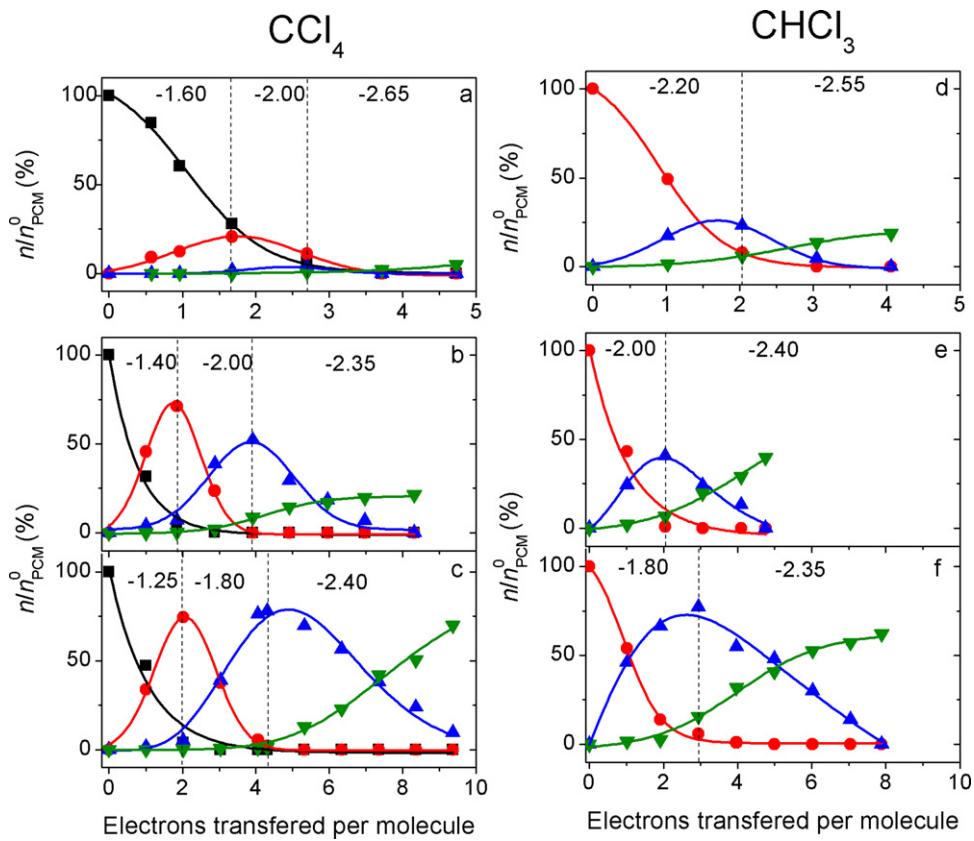
the final  $\text{CH}_4$  yield became 21.4% (Table 2, entries 3a–c). Further improvement of the results was observed when acetic acid was used as a proton source (Table 2, entries 5a–c). In this case 74.4% of  $\text{CHCl}_3$  and 78.0% of  $\text{CH}_2\text{Cl}_2$  were produced in the first and second steps of the electrolysis, respectively, while the last step yielded 70.0% of  $\text{CH}_4$ .

The theoretical charge consumption for the complete reduction of  $\text{CCl}_4$  to  $\text{CH}_4$  assuming a pure hydrodehalogenation mechanism is 8  $e^-$ /molecule, which means 2  $e^-$  for each leaving  $\text{Cl}^-$ . When no proton donor was added, 100% conversion of  $\text{CCl}_4$  and its  $\text{C}_1$

**Table 3**Electrolysis of  $\text{CHCl}_3$  (10 mM) in 20 mL DMF + 0.1 M  $\text{Pr}_4\text{NBF}_4$  at a Cu cathode.<sup>a</sup>

Entry	Substrate	$E_{\text{app}}^{\text{b}}$ (V)	$n^{\text{c}}$	$\text{CHCl}_3$ (%)	$\text{CH}_2\text{Cl}_2$ (%)	$\text{CH}_3\text{Cl}$ (%)	$\text{CH}_4$ (%)	$\text{C}_2^{\text{d}}$ (%)	$(\text{C}_1)_{\text{tot}}^{\text{e}}$ (%)
1a	$\text{CHCl}_3$	−2.20	2.0	8.0	23.1	0.3	6.0	1.4	37.4
1b		−2.55	4.0	0.0	0.0	0.1	18.6	3.0	18.7
2	$\text{CHCl}_3$	−2.55	2.1	17.7	1.0	0.1	6.2	0.6	25.0
		−2.55	3.6	0.0	0.0	0.3	16.4	1.4	16.7
3a	$\text{CHCl}_3 + \text{H}_2\text{O}^{\text{f}}$	−2.00	2.0	1.0	40.7	0.6	6.7	0.9	49.0
3b		−2.40	4.8	0.0	0.0	0.0	39.9	0.9	39.9
4	$\text{CHCl}_3 + \text{H}_2\text{O}^{\text{f}}$	−2.40	2.0	4.8	52.8	2.3	7.7	0.7	67.6
		−2.40	5.1	0.0	11.2	0.3	34.5	0.7	46.0
		−2.40	6.1	0.0	0.0	0.0	41.7	0.9	41.7
5a	$\text{CHCl}_3 + \text{HAc}^{\text{g}}$	−1.8	2.9	5.9	77.2	0.0	15.6	0.3	98.7
5b		−2.35	7.9	0.0	0	0.0	61.9	1.6	61.9
6	$\text{CHCl}_3 + \text{HAc}^{\text{g}}$	−2.35	3.1	10.7	65.5	2.5	11.4	0.3	90.1
		−2.35	8.2	0.0	22.1	0.6	64.7	1.2	87.4
		−2.35	10.4	0.0	0.0	0.0	72.4	1.7	72.4

<sup>a</sup> Values in percentage were calculated with respect to the starting substrate.<sup>b</sup> Applied potential vs. SCE.<sup>c</sup> Electrons transferred per molecule.<sup>d</sup>  $\text{C}_2$  stands for the sum of  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{H}_4$ .<sup>e</sup> Mass balance for  $\text{C}_1$  compounds with respect to initial substrate.<sup>f</sup> In the presence of 0.4 M  $\text{H}_2\text{O}$ .<sup>g</sup> In the presence of 0.1 M HAc.



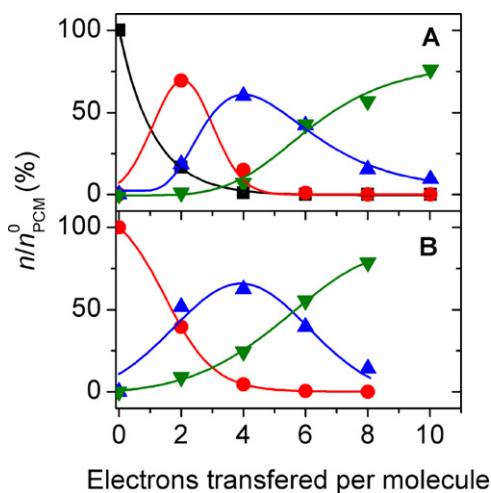
**Fig. 3.** Stepwise controlled-potential electrolyses of 10 mM  $\text{CCl}_4$  (a–c) and  $\text{CHCl}_3$  (D–F) at Cu in DMF + 0.1 M  $\text{Pr}_4\text{NBF}_4$  in the absence of added proton donors (a and d), or in the presence of 0.4 M  $\text{H}_2\text{O}$  (b and e) or 0.1 M HAc (c and f): (■)  $\text{CCl}_4$ , (●)  $\text{CHCl}_3$ , (▲)  $\text{CH}_2\text{Cl}_2$ , (▼)  $\text{CH}_4$ . The inserted numbers indicate  $E_{\text{app}}$ , whereas the vertical lines indicate when it was changed.

reduction intermediates was achieved with a charge consumption of  $4.7 \text{ e}^-/\text{molecule}$  (Table 2, entry 1c). The mass balance at the end of this experiment was very small. Addition of proton donors increased the charge consumption to values near to or slightly above the theoretical  $8 \text{ e}^-/\text{molecule}$  and significantly improved the mass balance (Table 2, compare entries 1, 3 and 5). The low charge consumption and the loss of carbon mass balance observed during electrolysis without added proton donors suggest that the mechanism cannot be a simple hydrodechlorination process, but involves other reaction pathways based on carbenes and radicals. Halogenated  $\text{C}_2$  compounds were not detected, whereas traces of ethane and ethylene were found (<2%) (Table 2, column 10). Therefore, dimerization of halogenated radicals or carbenes to give  $\text{C}_2$  is not a fundamental reaction pathway. In a previous research, carried out at GC and Ag electrodes, reactions of halocarbenes with DMF were proposed to be the principal route responsible for the mass balance loss. In fact, halocarbenes react rapidly with DMF to give CO and (halomethyl) dimethylamine [45].

Electrolyses of  $\text{CHCl}_3$  at Cu show similar trends as those described for  $\text{CCl}_4$ . The results are summarized in Table 3 and Fig. 3d–f. When the electrolysis was carried out at  $E_{\text{app}} = -2.20 \text{ V}$  vs. SCE without added proton donors,  $\text{CHCl}_3$  was mainly reduced to  $\text{CH}_2\text{Cl}_2$ , which was then transformed into  $\text{CH}_4$  at the second stage of the electrolysis performed at  $-2.55 \text{ V}$  vs. SCE (Fig. 3d and Table 3, entry 1). As in the case of  $\text{CCl}_4$ , the yields of hydrodehalogenated compounds as well as the overall carbon mass balance were quite low. It is particularly interesting to note that during the electrolysis at the first step ( $E_{\text{app}} = -2.20 \text{ V}$ ), a small amount of  $\text{CH}_4$  (6%) was produced (Table 3, entry 1a). This finding suggests the presence of a reaction route, possibly via carbene, not involving  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{Cl}$  as neither of them is reducible in these conditions.

When, instead, the electrolysis was performed in the presence of excess  $\text{H}_2\text{O}$  (Fig. 3e) or HAc (Fig. 3f), sequential hydrodechlorination of  $\text{CHCl}_3$  became the principal reduction route giving good yields of  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_4$  in the first and second steps, respectively. For example, the maximum yield of  $\text{CH}_2\text{Cl}_2$  obtained from the electrolysis at the first step increased from 23.1% in the absence of any added proton donor to 40.7% and 77.2% in the presence of  $\text{H}_2\text{O}$  and HAc, respectively (Table 3, compare entries 1a, 3a and 5a). Similarly, the yield of  $\text{CH}_4$  at the second step of electrolyses increased from 18.6% obtained in the absence of added proton donors to 39.9% and 61.9% when the electrolysis was performed in the presence of  $\text{H}_2\text{O}$  and HAc, respectively (Table 3, compare entries 1b, 3b and 5b).

The above results show that  $\text{CCl}_4$  and  $\text{CHCl}_3$  can be sequentially reduced to less chlorinated methanes and ultimately to  $\text{CH}_4$  by appropriately choosing the applied potential. If the goal is to convert  $\text{CCl}_4$  or  $\text{CHCl}_3$  to  $\text{CH}_4$ , a single step potentiostatic electrolysis may be more appropriate than a multi-step electrolysis. Some electrolyses of  $\text{CCl}_4$  and  $\text{CHCl}_3$  were carried out at Cu at a fixed potential corresponding to the last peak of each compound and the results are reported in Fig. S3 and Tables 2 and 3 (entries 2, 4 and 6). The results of these electrolyses are very similar to those obtained from multi-step potentiostatic experiments, both in terms of product distribution and charge consumption. However, one step electrolysis has the advantage of working with higher current density as compared to multi-step electrolyses and hence the experiment lasts in a much shorter time. As in the multi-step experiments, the concentrations of all intermediates as well as that of methane depend on the charge consumed during electrolysis. In the case of  $\text{CCl}_4$  reduction, accumulation of  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  is less favorable as compared to the sequential electrolysis because at the applied potential the starting substrate and all its reduction intermediates



**Fig. 4.** Galvanostatic electrolyses of (A)  $\text{CCl}_4$  ( $2.5 \text{ mA cm}^{-2}$ ) and (B)  $\text{CHCl}_3$  ( $2.0 \text{ mA cm}^{-2}$ ) at Cu in  $\text{DMF} + 0.1 \text{ M } \text{Pr}_4\text{NBF}_4 + 0.1 \text{ M HAc}$ ;  $c = 10 \text{ mM}$ ; (■)  $\text{CCl}_4$ , (●)  $\text{CHCl}_3$ , (▲)  $\text{CH}_2\text{Cl}_2$ , (▼)  $\text{CH}_4$ .

are reduced simultaneously. Chloromethane was also detected but always in a very low percentage. The final  $\text{CH}_4$  yield is affected by how reduction of  $\text{CCl}_4$  is accomplished (stepwise conversion to dechlorinated compounds up to  $\text{CH}_4$  versus instantaneous reduction of all intermediates) (Table 2, column 9). In any case, the yield of  $\text{CH}_4$  was quite low (<10%) when no acid was added into the reaction medium (Table 2, entries 1c and 2). Conversely, when the electrolysis was performed in the presence of acetic acid a very high yield of  $\text{CH}_4$  was obtained (Table 2, entries 5c and 6). It is important to stress that production of  $\text{CH}_4$  starts at the beginning of the electrolysis and steadily increases during the experiment, especially in the presence of acetic acid (Fig. S3c). In the case of the one-step electrolysis of  $\text{CHCl}_3$  (Table 3, entries 2, 4, 6 and Fig. S3d–f), the results are comparable with those of the stepwise electrolysis both in terms of accumulation of the intermediates and  $\text{CH}_4$  yield.

A last comment on these potentiostatic electrolyses is on the production of ethane and ethylene, which presumably arise from coupling reactions involving radicals or carbenes. These products were always detected at trace levels and their formation seems not to be really influenced by either the nature of the starting reagent  $\text{CCl}_4$  or  $\text{CHCl}_3$ , or the presence of  $\text{H}_2\text{O}$  or  $\text{HAc}$ . The independence of the yields of these  $\text{C}_2$  hydrocarbons on the proton availability of the medium may be taken to be supportive of a radical mechanism for their formation. In fact, formation of carbenes via expulsion of  $\text{Cl}^-$  from  $-\text{CH}_n\text{Cl}_{(3-n)}$  is in competition with protonation (Eqs. (3) and (4)), which means that the fraction of the electrogenerated carbanion evolving toward side products via carbene should decrease in the presence of a good proton donor. On the other hand, neither formation of radicals nor their conversion appears to be affected by protons.

Galvanostatic electrolysis is often more simple and more preferable than the potentiostatic one, especially if large-scale applications are to be considered. We therefore checked the efficiency of the Cu electrode under galvanostatic conditions to complete the series of the preparative-scale experiments on the reductive cleavage of polychlorinated methanes. Galvanostatic electrolyses of  $\text{CCl}_4$  and  $\text{CHCl}_3$  were performed at  $2.5$  and  $2.0 \text{ mA cm}^{-2}$ , respectively. The experiments were performed in the presence of  $0.1 \text{ M HAc}$ . The concentration profiles of  $\text{CCl}_4$  and  $\text{CHCl}_3$  as well as their reduction intermediates and products observed during galvanostatic electrolyses are illustrated in Fig. 4. In good agreement with the results of the controlled-potential electrolyses, the principal reduction intermediates of  $\text{CCl}_4$  were  $\text{CHCl}_3$  (maximum 70%) and  $\text{CH}_2\text{Cl}_2$  (maximum 60%), whereas

galvanostatic reduction of  $\text{CHCl}_3$  showed formation of  $\text{CH}_2\text{Cl}_2$  (maximum 62%) as the only detectable intermediate. In both cases, however, the final conversion of the polychloromethane to  $\text{CH}_4$  was ca. 80%, whereas the charge consumption was comparable with that already observed for the controlled-potential electrolyses.

#### 4. Environmental and economical relevance

Copper is one of the most abundant metals present on the earth's crust and is immensely cheaper than Pt, Au, Pd and, most interestingly, Ag (10 times cheaper), which so far is the most active electrocatalytic material for the dehalogenation of organic halides. The most important outcome of this study is that Cu allows the degradation of highly toxic polychlorinated methanes to  $\text{CH}_4$  under fairly mild conditions. Another relevant outcome is that although Ag shows higher catalytic activities toward the reduction of PCMs with respect to Cu, the latter may be considered a good candidate to substitute Ag in large scale applications. The catalytic activity of Cu, as already observed for Ag, is enhanced by the presence of a good proton source, which probably accelerates the rate of regeneration of the active sites on the metal surface. In addition, the electrode remains active during long lasting electrolyses, which demonstrates its good resistance to poisoning.

Another interesting aspect is that also the final conversion of PCMs to  $\text{CH}_4$  is excellent, particularly when the electrolyses are carried out in the presence of acetic acid, although Ag has shown higher selectivity with respect to Cu both in the presence and absence of a proton donor (Fig. S4). Since PCMs are highly soluble in dipolar solvents such as DMF or acetonitrile, they could be transferred from the contaminated sites (via gas bubbling or sequestering agents) to an organic solvent and successively electrolyzed at catalytic electrodes such as Cu to produce  $\text{CH}_4$ . Therefore, an electrochemical method employing Cu bears an important environmental significance; it affords the basis for developing reductive destruction methods at relatively cheap electrodes in combination with physical removal of PCMs from contaminated wastewaters. This is a particularly interesting point if we consider that the dehalogenation process may be coupled with a combustion process in which the thermal energy can be recycled to produce electric energy. The possibility to recycle energy from the degradation process allows to abate the treatment costs and therefore make this process interesting also from a commercial point of view.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2012.07.004>.

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